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Reactivity of the Dinuclear Rhodium(II) Complex [C5Me5Rh(μ-PMe2)]2 toward Chalcogens and Alkynes. An Example of Double Insertion of Oxygen into Two Rh–PMe2 Bonds[1]

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The complex [C5Me5Rh(μ-PMe2)]2 (2) reacts with oxygen, sulfur, selenium, and tellurium to give three different types of products, [C5Me5Rh(μ-OPMe2)2RhC5Me5] (3), [(C5Me5Rh)2(μ-PMe2)(μ-EPMe2)] (4, E = S; 6, E = Se), and [(C5Me5Rh)2(μ-PMe2)2(μ-E)] (5, E = Se; 7, E = Te), which originate from addition of a chalcogen to the Rh–Rh bond or insertion into one or two of the Rh–P bonds. The crystal and molecular structure of 7 has been determined. Crystal data for 7: monoclinic, $P2_1/c$, $a = 11.208$ (2) Å, $b = 17.079$ (4) Å, $c = 15.286$ (4) Å, $\beta = 106.93$ (2)°, $V = 2799.1$ (12) Å^3, $Z = 4$, and $R(F) = 5.04\%$, for 3808 reflections with $F_0 \geq 3.0\sigma(F_0)$. The nucleophilic behavior of the bridging chalcogen atoms in the complexes 5 and 7 has been characterized by their reaction with methyl iodide, which gives almost quantitatively the ionic compounds [(C5Me5Rh)2(μ-PMe2)2(μ-ECH3)]I (8, 9). Complex 2 reacts with C2(CO2Me)2 to form two isomeric products, [(C5Me5Rh)2(μ-PMe2)(μ-PMe2C2(CO2Me)2)] (10) and [(C5Me5Rh)2(μ-PMe2C(CO2Me)=C(CO2Me)PMe2)] (11), which are not interconvertible and the second of which contains a chelating as well as bridging 1,2-bis(dimethylphosphino)ethene ligand.

In the last decade there has been an increasing interest in the chemistry of phosphido-bridged transition-metal complexes.[2,3] The main reason for this is that the PR2 group, in contrast to other ligands such as CO, chloride, or hydride, usually behaves as a stable bridging unit; therefore, complexes having M–PR2–M bridges in most cases show a reduced tendency to fragment into monometallic species.

More recently, this general assumption that phosphido bridges are inert has had to be modified, and there are now numerous examples (vide infra) of insertion into or reactivity at the bridge. Following the discovery that not only the mononuclear compound C5H5Co(PMe3)2 but also the dinuclear complex [C5H5Co(μ-PMe2)]2 (1) are easily protonated to give the hydrido-bridged dicobalt cation [(C5H5Co)2(μ-PMe2)2(μ-H)]+,[4] we found that electrophiles such as CH2Br2 or CH2I2 react with 1 either by oxidative addition or insertion of the CH2 unit into one of the Co–PMe2–Co bonds. The dimethylphosphido bridge can thus be expanded into a CH2PMe2 unit, which provides more flexibility to the molecule. The insertion of a CH2 or a substituted methylene unit into a PR2 bridge is certainly not limited to cobalt compounds as recent studies, particularly by Wojcicki[5] and Geoffroy et al.,[6] have shown that iron and osmium complexes behave similarly.

The above-mentioned dual reactivity of the dicobalt compound 1 when treated with electrophiles has also been observed in the reaction with sulfur, selenium, and tellurium. Depending on the chalcogen atom, oxidative addition and/or insertion occurs.[7] In order to find out whether this is a more general phenomenon, we recently prepared the C5Me5/rhodium analogue of 1, [C5Me5Rh(μ-PMe2)]2 (2), and first studied the protonation reaction of this complex.[1,8] The present paper describes the behavior of 2 toward oxygen and its congeners and also reports on an insertion reaction that takes place in the presence of C2(CO2Me)2. A short communication with some preliminary results of this work has already appeared.[9]

Results

Addition and Insertion Reactions of Oxygen, Sulfur, Selenium, and Tellurium.
The rhodium compound 2 reacts with the chalcogens under conditions similar to those that have been used for the reactions of the cobalt analogue 1. The important difference is, however, that (1) *oxygen* forms a product in which the dinuclear framework of the starting material has been retained and (2) in contrast to the cobalt case, three different types of compounds are formed (see Scheme I).

The reaction of 2 with oxygen to produce 3 takes place by bubbling O2 through a benzene solution at room temperature. This

procedure gives much better yields than stirring a solution of 2 in air for a longer period of time. In accord with the NMR spectroscopic data (see Table I), there is not doubt that an *unsymmetrical* complex is formed that has two different C5Me5Rh units. We therefore assume that the O2 molecules primarily interacts with one metal center only and that this interaction weakens the oxygen–oxygen bond, finally leading to an insertion of the oxygen atoms into two Rh–PMe2 bonds *on the same side* of the molecule.[19] There is a striking similarity between 3 and the dinuclear cation [C5Me5Rh(μ-OPR2)3RhC5Me5]+ (R = OMe) recently described by Kläui et al.[10] in which the oxygens of the three bridging OPR2 groups are also linked to the *same* rhodium atom.

The most reactive of the chalcogens toward 2 is sulfur S8. Complete reaction in benzene at room temperature occurs in a few minutes; even if an excess of S8 is used, only complex 4 is produced. The presence of two nonequivalent PMe2 groups is clearly indicated in the 31P NMR spectrum, which shows two signals with a large difference in chemical shift and also in coupling constants. Although complex 4 still contains an unchanged Rh–PMe2–Rh fragment, as is present in 2, it does not react with O2 to give a OPMe2- and SPMe2-bridged dinuclear compound.

The reaction of 2 with selenium gives a mixture of products, of which 5 and 6 can be separated by chromatographic techniques. Whereas complex 5 is a symmetrical molecule formed by insertion of a selenium atom into the metal–metal bond, the second product, 6, is structurally related to 4 and contains both a PMe2 and a SePMe2 bridging unit. Similarly, treatment of 1 with selenium also forms two compounds of composition [(C5H5Co)2(μ-PMe2)2(μ-Se)] and [(C5H5Co)2(μ-PMe2)(μ-SePMe2)], the amount

(1) Part 9 of the series Metal Complexes with Bridging Dimethylphosphido Ligands. Part 8: Klingert, B.; Werner, H. *J. Organomet. Chem.*, in press.
(2) Vahrenkamp, H. *Angew. Chem.* **1978**, *90*, 403; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.
(3) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163; *Pure Appl. Chem.* **1982**, *54*, 113.
(4) (a) Werner, H.; Hofmann, W. *Angew. Chem.* **1979**, *91*, 172; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 158. (b) Werner, H.; Hofmann, W.; Zolk, R.; Dahl, L. F.; Kocal, J.; Kühn, A. *J. Organomet. Chem.* **1985**, *289*, 173.
(5) (a) Yu, Y.-F.; Chau, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3704. (b) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Chem. Soc., Chem. Commun.* **1984**, 653. (c) Yu, Y.-F.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1986**, *5*, 47.
(6) (a) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519.
(7) (a) Hofmann, W.; Werner, H. *Angew. Chem.* **1981**, *93*, 1088; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1014. (b) Werner, H.; Luxenburger, G.; Hofmann, W.; Nadvornik, M. *J. Organomet. Chem.* **1987**, *323*, 161.
(8) Werner, H.; Klingert, B.; Rheingold, A. L. *Organometallics*, in press.
(9) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.
(10) Kläui, W.; Otto, H.; Eberspach, W.; Buchholz, E. *Chem. Ber.* **1982**, *115*, 1922.

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Scheme I
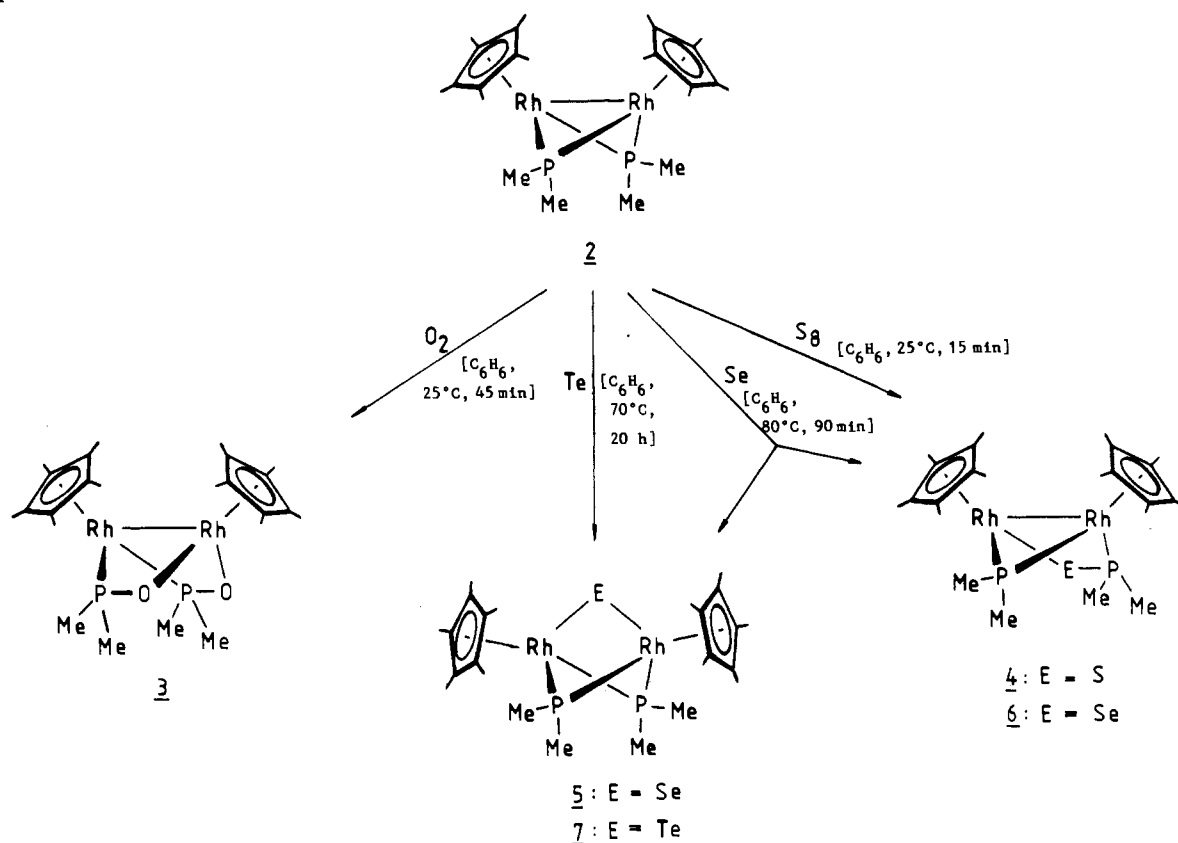
Table I. ¹H and ³¹P NMR Data for 3–9ᵃ

	δ(C5Me5) [J_{P-H}, Hz]	δ(PMe2/EPMe2) [N, Hz]	δ(PMe2) [J_{Rh-P}, Hz; J_{P-P}, Hz]	δ(EPMe2) [J_{Rh-P}, Hz; J_{P-P}, Hz]
3	1.95 (dt)ᵇ [2.2] 1.67 (s)	1.72 (vt) [9.6] 1.48 (vt) [8.8]		75.30 (dd) [156.6, 2.2; g]
4	1.95ᶜ	d	118.25 (dt) [150.4; 19.4]	9.37 (ddd) [160.8, 6.0; 19.4]
5	1.90 (t) [2.6]	2.10 (tvt)ᵉ [11.6] 1.50 (tvt) [9.0]	−84.53 (t) [97.6; g]	
6	2.00 (dd)ᵇ [1.9] 1.93 (ddd)ᵇ [2.8, 1.4]	d	118.12 (ddd) [152.6, 148.1; 14.9]	−15.61 (ddd) [165.2, 7.4; 14.9]
7	1.93 (t) [2.6]	2.15 (vt) [11.6] 1.46 (vt) [9.0]	−96.53 (t) [96.8]	
8	1.95 (t) [2.6]	f	−90.91 (dt) [94.7; 200.4] −67.06 (dt) [94.7; 200.4]	
9	1.95 (t) [2.6]	f	−91.06 (dt) [92.3; 200.0] −73.50 (dt) [92.3; 200.0]	

ᵃSpectra of 3–7 in C6D6; spectra of 8 and 9 in CD3NO2. ¹H, Me4Si internal standard; ³¹P, 85% H3PO4 external standard. Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, and vt = virtual triplet. ᵇJ_{Rh-H} = 0.5 Hz. ᶜComplex pattern due to overlap of the two C5Me5 signals. ᵈComplex pattern due to overlap of the four doublets of the four nonequivalent PCH3 groups. ᵉJ_{Rh-H} = 1.0 Hz. ᶠComplex pattern due to overlap of the signals of the four nonequivalent PCH3 groups and the signal of the ECH3 protons. ᵍNot observed.

of which strictly depends on the type of selenium used.[7] The NMR data for **6** are similar to those for **4**, showing, by ¹H NMR, the presence of two different C5Me5 Rh units. One of the respective signals is a doublet of doublets, whereas the other corresponds to a doublet of doublet of doublets due to coupling of the CH3 protons to rhodium and two *different* phosphorus atoms. Other transition-metal complexes containing a M(μ-EPR2)M unit (E = S or Se) are known but have been prepared not by insertion of sulfur or selenium into a M-PR2-M bridge but by reaction of a suitable starting material with either R2P(E)P(E)R2 or with secondary phosphine chalcogenides HP(E)R2.[11,12]

The least reactive of the chalcogens expectedly is Te. The reaction of **2** with finely powdered tellurium in benzene at 70 °C after 20 h again gives a mixture of products from which **7** has been isolated as dark brown crystals in 74% yield. The presence of two signals of equal intensity for the PCH3 protons in the ¹H NMR spectrum of **7** indicates that the Rh2P2 four-membered ring is *not planar*, a fact confirmed by X-ray analysis. The appearance of the ³¹P NMR signal in the high-field region is in agreement with the absence of a metal–metal bond in this molecule.

The formation of the analogous complexes **5** and **7** is best understood by assuming that the metal base **2** attacks the chalcogen as a nucleophile leading to degradation of the Eₙ chain and finally to insertion of a chalcogen atom into the metal–metal bond. There is precedent for this process in the dinuclear palladium and platinum compounds [M2Cl2(μ-dppm)2] (M = Pd, Pt; dppm =

(11) (a) Wagner, K. P.; Hess, R. W.; Treichel, P. M.; Calabrese, J. C. *Inorg. Chem.* **1975**, *14*, 1121. (b) Boag, N. M.; Browning, J.; Crocker, C.; Goggin, P. L.; Goodfellow, R. J.; Murray, M.; Spencer, J. L. *J. Chem. Res., Synop.* **1978**, 228; *J. Chem. Res., Miniprint* **1978**, 2962. (c) Messbauer, B.; Meyer, H.; Walther, B.; Heeg, M. J.; Maqsudur Rahman, A. F. M.; Oliver, J. P. *Inorg. Chem.* **1983**, *22*, 272. (d) Anderson, D. M.; Ebsworth, E. A. V.; Stephenson, T. A.; Walkinshaw, M. D. *J. Chem. Soc., Dalton Trans.* **1982**, 2343.

(12) (a) Lindner, E.; Bouachir, F.; Hoehne, S. *Chem. Ber.* **1983**, *116*, 46. (b) Kläui, W.; Schmidt, K.; Bockmann, A.; Hofmann, P.; Schmidt, H. R.; Stauffert, P. *J. Organomet. Chem.* **1985**, *286*, 407.

Scheme II
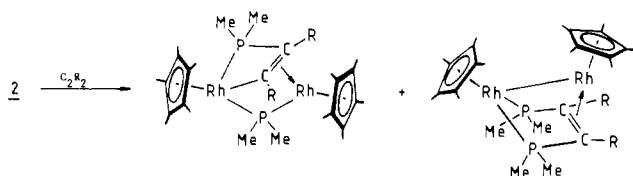
$CH_2(PPh_2)_2)$, which also react with sulfur via cleavage of the M–M bond to give $[M_2Cl_2(\mu\text{-dppm})_2(\mu\text{-S})]$,[13] whereas the dinuclear rhodium complex $[C_5Me_5Rh(\mu\text{-CO})]_2$ is transformed by addition of Se to give a selenium-bridged product, $[(C_5Me_5)_2\text{-}(CO)_2Rh_2(\mu\text{-Se})]$.[14]

Methylation Reaction of 5 and 7. As the selenium and tellurium atoms in compounds 5 and 7 still contain two nonbonding electron pairs, the addition of an electrophile to the chalcogen bridge should be possible. Accordingly, 5 and 7 react with methyl iodide to produce almost quantitatively complexes 8 and 9, which have been

8, E = Se; 9, E = Te
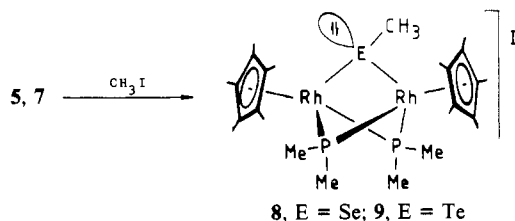
characterized by elemental analysis and NMR data (Table I). The ionic products, which form yellow air-stable crystals, are 1:1 electrolytes in nitromethane solution.

In contrast to those of 5 and 7, the ^{31}P NMR spectra of 8 and 9 show two signals illustrating the stereochemical nonequivalence of the two PMe_2 units. Similar protonation and methylation reactions of bridging chalcogen atoms also occur in the case of the dinuclear cobalt compounds $[(C_5H_5Co)_2(\mu\text{-PMe}_2)_2(\mu\text{-E})]$ (E = S, Se, Te),[7] as well as with the dichromium complex $[(C_5H_5Cr)_2(\mu\text{-S-}t\text{-Bu})_2(\mu\text{-S})]$.[15] It should finally be noted that the isomer of 5, compound 6, does not react with methyl iodide by electrophilic addition to form a cationic $Rh\text{-SeMe-PMe}_2\text{-}Rh$-bridged species.

Reactions of 2 with Alkynes. The unexpected ability of M–PR_2–M bridging fragments to insert CH_2 or alkynes, as mentioned earlier, has also been found by using 2 as the starting material. Although the dinuclear complex is inert toward acetylene and but-2-yne, it smoothly reacts with $C_2(CO_2Me)_2$ to give two products, 10 and 11, which have been separated by column chromatography. These compounds are isomers but differ remarkably in color (10, orange; 11, red violet) and spectroscopic properties. From the ^1H NMR data (see Experimental Section), there is no doubt that in both isomers two different C_5Me_5Rh units are present. The spectrum of 10 contains one C_5Me_5 signal showing coupling to two phosphorus atoms and one showing coupling only to one ^{31}P, which is in agreement with the structure proposed in Scheme II. The mechanism of formation of 10 is probably similar to that of the $EPMe_2$-bridged compounds 4 and 5, indicating that S and Se, as well as $C_2(CO_2Me)_2$, behave as electrophiles. Previous examples of the insertion of an alkyne molecule into one M–PR_2 bond of a M–PR_2–M bridging unit include the formation of $[C_5H_5Ni(\mu\text{-PPh}_2CPh=CPh)Fe(CO)_3]$ from $[C_5H_5Ni(\mu\text{-CO})(\mu\text{-PPh}_2)Fe(CO)_3]$ and C_2Ph_2[16] and the
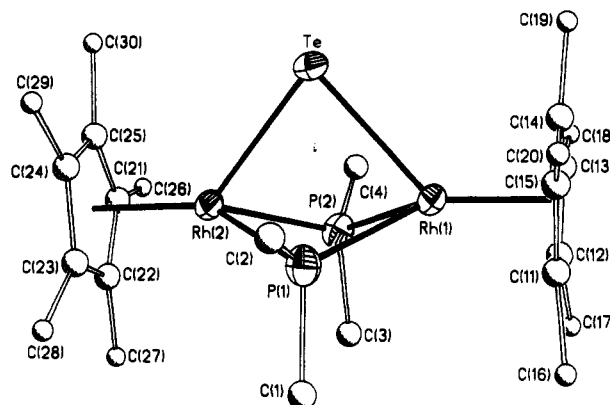

Figure 1. Molecular structure and labeling scheme for $[(C_5Me_5Rh)_2(\mu\text{-PMe}_2)_2(\mu\text{-Te})]$ (7) with 40% probability thermal ellipsoids.
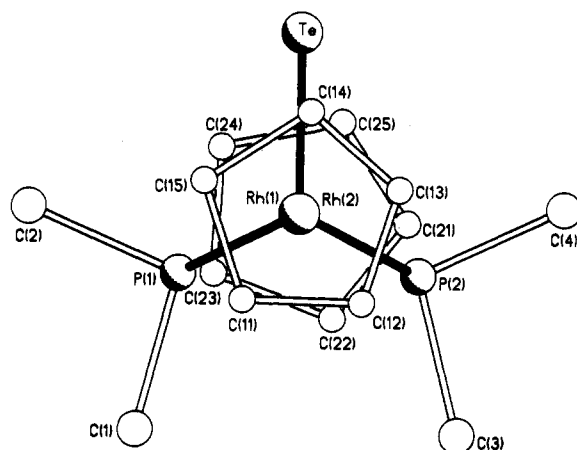

Figure 2. Structure of 7 viewed down the Rh···Rh vector and drawn without perspective.

formation of $[(CO)_3Ru(\mu\text{-CO})(\mu\text{-PPh}_2CPh=CPh)Co(CO)_2]$ from $[(CO)_4Ru(\mu\text{-PPh}_2)Co(CO)_3]$ and C_2Ph_2,[17] respectively.

The NMR spectroscopic data of 11 point to a higher degree of symmetry for this complex as compared to 10. In the ^1H NMR spectrum there are only two virtual triplets for the PCH_3 protons and one singlet for the CO_2Me groups. Furthermore, of the two C_5Me_5 signals, only one shows PH coupling to two equivalent ^{31}P nuclei. We therefore assume that, by insertion of a $C_2(CO_2Me)_2$ molecule into the two Rh–PMe_2 bonds of one rhodium atom of 2, a 1,2-bis(dimethylphosphino)ethene ligand is produced, which is linked as a chelating as well as a bridging ligand to the two metal centers and behaves as a six-electron donor group. The analogue of compound 11 having two C_5H_5Co instead of two C_5Me_5Rh fragments is formed as the final product in the reaction of 1 with $C_2(CO_2Me)_2$ and has been characterized by X-ray analysis.[18] It should be noted that the less symmetrical complex 10 is probably not an intermediate in the formation of 11 as heating a benzene solution of 10 under a reflux for 24 h does not lead to any change.

Crystal and Molecular Structure of 7. $[(C_5Me_5Rh)_2(\mu\text{-PMe}_2)_2(\mu\text{-Te})]$ (7) crystallizes as discrete molecules (Figure 1) containing two C_5Me_5Rh units triply bridged by two dimethylphosphido groups and a Te atom; the bridges are not supported by a Rh–Rh bond (Rh···Rh = 3.423 (1) Å). The Cp* rings are nearly coplanar; the planes, which are inclined away from the Te atom, are related by an angle of 4.5 (1)°, and the centroid–Rh–Rh–centroid dihedral angle is –19.0 (1)°. The molecule ap-

(13) (a) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979,** *18*, 2996. (b) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979,** *18*, 2808.

(14) Herrmann, W. A.; Bauer, C.; Weichmann, J. *Chem. Ber.* **1984,** *117*, 1271.

(15) Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Rakitin, Yu. V.; Novotortsev, V. M.; Ellert, O. G.; Kalinnikov, V. T. *Inorg. Chim. Acta* **1980,** *39*, 91.

(16) (a) Yasufuku, K.; Yamazaki, H. *J. Organomet. Chem.* **1972,** *35*, 367. (b) Yasufuku, K.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1975,** *84*, C28. (c) Barnett, B. L.; Krüger, C. *Cryst. Struct. Commun.* **1973,** *2*, 347.

(17) (a) Smith, W. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1976,** 896. (b) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984,** *3*, 814.

(18) Werner, H.; Zolk, R. *Chem. Ber.* **1987,** *120*, 1003.

(19) A reviewer has proposed an alternative mechanism: The insertion of the first oxygen atom gives a $\mu\text{-Me}_2P=O$ ligand, which has a strong cis labilizing effect on the second phosphido bridge. Therefore, the second oxygen inserts into the Rh–P bond at the same Rh atom where the oxygen of the $\mu\text{-Me}_2$ is coordinated.

proximates C_{2v} symmetry, which is broken only by the rotational orientations of the Cp* rings (Figure 2). The Te atom functions as only a two-electron donor, confirmed by its observed ease of reaction with electrophiles.

Experimental Section

All reactions were carried out in Schlenk tubes under an atmosphere of nitrogen. The starting complex **2** was prepared by the literature method.[8] Sulfur, selenium, and tellurium as well as $C_2(CO_2Me)_2$ were obtained from commercial sources.

Preparation of [C₅Me₅Rh(μ-OPMe₂)₂RhC₅Me₅] (3). Oxygen was bubbled into a benzene solution (5 mL) of **2** (200 mg, 0.33 mmol) at room temperature for 45 min. After the solvent was removed, the residue was extracted with pentane (10 mL). The solution was filtered and the filtrated was concentrated in vacuo. Cooling to −78 °C gave red-brown crystals, which were washed with pentane (−78 °C) and dried in vacuo: yield 65 mg (31%); mp 215 °C dec. Anal. Calcd for $C_{24}H_{42}O_2P_2Rh_2$: C, 45.73; H, 6.72; Rh, 32.65. Found: C, 45.36; H, 6.80; Rh, 32.41. IR (KBr): ν(PO) = 990 cm⁻¹. MS (70 eV): m/e 630 (100%; M⁺), 614 (8%; M⁺ − O), 598 (4%; M⁺ − 2O), 552 (10%; M⁺ − HP(O)Me₂), 495 (13%; M⁺ − C₅Me₅), 474 (13%; [C₅Me₄CH₂Rh]₂⁺), 373 (33%; Rh-(C₅Me₅)₂⁺), 315 (13%; C₅Me₅RhP(O)Me₂⁺), 237 (33%; C₅Me₄CH₂Rh⁺).

Preparation of [(C₅Me₅Rh)₂(μ-PMe₂)(μ-SPMe₂)] (4). A benzene solution (5 mL) of **2** (200 mg, 0.33 mmol) was treated with sulfur S₈ (14 mg, 0.055 mmol) and stirred for 15 min at room temperature. Workup as described for **3** led to the formation of red crystals: yield 45 mg (22%); mp 130 °C dec. Anal. Calcd for $C_{24}H_{42}P_2Rh_2S$: C, 45.73; H, 6.72; Rh, 32.65. Found: C, 45.63; H, 6.85; Rh, 32.54. IR (KBr): ν(PS) = 550 cm⁻¹. MS (70 eV): m/e 630 (59%; M⁺), 569 (100%; M⁺ − PMe₂), 331 (34%; C₅Me₅RhSPMe₂⁺), 237 (20%; C₅Me₄CH₂Rh⁺).

Preparation of [(C₅Me₅Rh)₂(μ-PMe₂)(μ-SePMe₂)] (5) and [(C₅Me₅Rh)₂(μ-PMe₂)₂(μ-Se)] (6). A benzene solution (5 mL) of **2** (250 mg, 0.42 mmol) was treated with gray selenium (40 mg, 0.50 mmol) and stirred at 80 °C for 90 min. After the mixture had cooled to room temperature, the solvent was removed and the residue dissolved in pentane (10 mL). The solution was chromatographed on Al₂O₃ (neutral, activity grade V) to give the pentane a red-brown fraction from which dark-brown crystals of **5** were isolated after concentration of the solution and cooling to −78 °C. With ether, a second brown fraction was eluted that contained **6** and was worked up as described for **5**.

5: yield 117 mg (41%); mp 220 °C dec. Anal. Calcd for $C_{24}H_{42}P_2Rh_2Se$: C, 42.56; H, 6.25; Rh, 30.39. Found: C, 42.14; H, 6.40; Rh, 30.29. MS (70 eV): m/e 678 (58%; M⁺), 617 (100%; M⁺ − PMe₂), 379 (13%; C₅Me₅RhSePMe₂⁺), 237 (14%; C₅Me₄CH₂Rh⁺).

6: yield 31 mg (11%); mp 300 °C dec. Anal. Calcd for $C_{24}H_{42}P_2Rh_2Se$: C, 42.56; H, 6.25; Rh, 30.39. Found: C, 42.31; H, 6.39; Rh, 30.25. MS (70 eV): m/e 678 (48%; M⁺), 617 (100%; M⁺ − PMe₂), 379 (10%; C₅Me₅RhSePMe₂⁺), 237 (9%; C₅Me₄CH₂Rh⁺).

Preparation of [(C₅Me₅Rh)₂(μ-PMe₂)₂(μ-Te)] (7). A benzene solution (5 mL) of **2** (150 mg, 0.25 mmol) was treated with finely powered tellurium (44 mg, 0.35 mmol) and stirred at 70 °C for 20 h. After the mixture had cooled to room temperature, the solvent was removed and the residue dissolved in toluene (10 mL). The solution was chromatographed on Al₂O₃ (neutral, activity grade V) to give finally dark-brown crystals, which were washed with pentane and dried in vacuo: yield 134 mg (74%); mp 300 °C dec. Anal. Calcd for $C_{24}H_{42}P_2Rh_2Te$: C, 39.71; H, 5.83; Rh, 28.35. Found: C, 39.83; H, 5.78; Rh, 28.13. MS (70 eV): m/e 728 (71%; M⁺), 667 (100%; M⁺ − PMe₂), 429 (4%; C₅Me₅RhTePMe₂⁺), 237 (7%; C₅Me₄CH₂Rh⁺).

Preparation of [(C₅Me₅Rh)₂(μ-PMe₂)₂(μ-ECH₃)]I (8, E = Se; 9, E = Te). A suspension of **6** or **7** (0.1 mmol) in ether (10 mL) was treated with methyl iodide (21 mg, 0.15 mmol) and stirred for 10 min at room temperature. A yellow precipitate was formed, which was filtered off, washed with ether and pentane, and dried in vacuo; yield 95%.

8: mp 250 °C dec; equivalent conductivity (CH₃NO₂), Λ = 78 cm² Ω⁻¹ mol⁻¹. Anal. Calcd for $C_{25}H_{45}IP_2Rh_2Se$: C, 36.65; H, 5.54; Rh, 25.12. Found: C, 36.54; H, 5.37; Rh, 24.94.

9: mp 230 °C dec; equivalent conductivity (CH₃NO₂), Λ = 76 cm² Ω⁻¹ mol⁻¹. Anal. Calcd for $C_{25}H_{45}IP_2Rh_2Te$: C, 34.60; H, 5.23; Rh, 23.71. Found: C, 34.37; H, 5.16; Rh, 23.33.

Preparation of [(C₅Me₅Rh)₂(μ-PMe₂)(μ-PMe₂C₂(CO₂Me))] (10) and [(C₅Me₅Rh)₂(μ-PMe₂C(CO₂Me)=C(CO₂Me)PMe₂)] (11). A benzene solution (5 mL) of **2** (250 mg, 0.42 mmol) was treated with $C_2(CO_2Me)_2$ (114 mg, 1.0 mmol) and stirred for 2 h at room temperature. After the solvent and excess alkyne were removed in vacuo, the residue was dissolved in hexane−ether 1:1 (10 mL) and chromatographed on Al₂O₃ (neutral, activity grade V). With ether−hexane 1:1, first a dark-brown fraction was obtained, which was brought to dryness and again chromatographed on Al₂O₃ with ether as the eluant. After the solvent was

Table II. Crystallographic Data for **7**

formula	$C_{24}H_{42}P_2Rh_2Te$
fw	725.6
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.208 (2)
b, Å	17.079 (4)
c, Å	15.286 (4)
β, deg	106.93 (2)
V, Å³	2799.1 (12)
Z	4
D(measd), g cm⁻³	1.72
D(calcd), g cm⁻³	1.722
color	deep red
size, mm	0.11 × 0.28 × 0.32
μ(Mo Kα), cm⁻¹	23.2
temp, K	293
T(max)/T(min)	0.951/0.641
diffractometer	Nicolet R3m/μ
radiation	Mo Kα (0.71073 Å)
monochromator	graphite
scan method	ω
scan limits, deg	$4 \leq 2\theta \leq 50$
octants collcd	$\pm h,k,l$
no. of reflcns collcd	5134
no. of indep reflcns	4798
R(int), %	3.30
no. of obsd reflcns ($3\sigma(F_o)$)	3808
std reflcns	3 std/197 reflcns
decay	∼10%
$R(F)$, %	5.04
$R(wF)$, %	5.85
GOF	1.561
Δ/σ	0.058
$\Delta(\rho)$, e Å⁻³	0.93 (1.3 Å from Te)
N_o/N_v	14.5

Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U^a
Te	−1487.9 (6)	3002.1 (5)	1383.4 (4)	64.9 (3)
Rh(1)	283.4 (6)	3809.2 (4)	2591.1 (4)	36.7 (2)
Rh(2)	−2803.2 (6)	3572.3 (4)	2437.8 (4)	38.3 (2)
P(1)	−1470 (2)	4565 (2)	2338 (2)	49 (1)
P(2)	−903 (2)	3277 (2)	3433 (2)	44 (1)
C(1)	−1372 (10)	5371 (6)	3153 (8)	81 (5)
C(2)	−1936 (11)	5124 (8)	1269 (8)	94 (6)
C(3)	−609 (10)	3659 (8)	4606 (6)	83 (5)
C(4)	−607 (11)	2242 (7)	3698 (9)	89 (6)
C(11)	1918 (9)	4568 (7)	2972 (8)	69 (5)
C(12)	2197 (10)	3921 (10)	3517 (8)	81 (5)
C(13)	2194 (9)	3299 (7)	2988 (10)	80 (5)
C(14)	1916 (9)	3507 (10)	2085 (9)	107 (7)
C(15)	1722 (9)	4337 (9)	2039 (8)	81 (5)
C(16)	1972 (15)	5434 (10)	3313 (18)	192 (14)
C(17)	2583 (12)	3984 (14)	4589 (8)	167 (11)
C(18)	2505 (15)	2463 (11)	3389 (20)	219 (16)
C(19)	1867 (16)	2973 (18)	1308 (18)	295 (19)
C(20)	1468 (14)	4829 (18)	1178 (14)	262 (17)
C(21)	−4231 (9)	2881 (7)	2886 (7)	68 (4)
C(22)	−4263 (9)	3650 (8)	3155 (7)	85 (5)
C(23)	−4622 (9)	4130 (6)	2319 (11)	92 (6)
C(24)	−4801 (8)	3605 (7)	1555 (7)	62 (4)
C(25)	−4543 (8)	2854 (6)	1953 (6)	54 (4)
C(26)	−3962 (14)	2154 (12)	3535 (11)	158 (10)
C(27)	−4098 (15)	3979 (15)	4086 (11)	206 (13)
C(28)	−4893 (13)	4987 (9)	2241 (19)	191 (14)
C(29)	−5188 (11)	3779 (12)	545 (9)	149 (10)
C(30)	−4672 (12)	2082 (8)	1398 (11)	110 (7)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

removed in vacuo, the residue was recrystallized from pentane (−78 °C) to give red violet crystals of **11**. The orange fraction that was eluted second was also brought to dryness, and the residue was recrystallized from pentane. Orange crystals of **10** were obtained.

10: yield 110 mg (35%); mp 200 °C dec. Anal. Calcd for $C_{30}H_{48}O_4P_2Rh_2$: C, 48.66; H, 6.53; Rh, 27.79. Found: C, 48.58; H,

Table IV. Selected Bond Distances and Angles for
[(C$_5$Me$_5$Rh)$_2$(μ-PMe$_2$)$_2$(μ-Te)] (7)

(a) Bond Distances (Å)

Rh(1)···Rh(2)	3.423 (1)	Rh(2)–P(1)	2.295 (3)
Rh(1)–CNT(1)^a	1.878 (11)	Rh(2)–P(2)	2.284 (2)
Rh(2)–CNT(2)	1.886 (11)	P(1)–C(1)	1.838 (12)
Rh(1)–Te	2.667 (1)	P(1)–C(2)	1.831 (12)
Rh(2)–Te	2.665 (1)	P(2)–C(3)	1.846 (10)
Rh(1)–P(1)	2.288 (3)	P(2)–C(4)	1.823 (11)
Rh(1)–P(2)	2.290 (3)	P(1)···P(2)	2.725 (4)

(b) Bond Angles (deg)

Rh(1)–Te–Rh(2)	79.91 (6)	CNT(2)–Rh(2)–Te	130.3 (1)
Rh(1)–P(1)–Rh(2)	96.6 (1)	CNT(2)–Rh(2)–P(1)	139.1 (2)
Rh(1)–P(2)–Rh(2)	96.9 (1)	CNT(2)–Rh(2)–P(2)	137.2 (2)
CNT(1)–Rh(1)–Te	131.4 (1)	Te–Rh(2)–P(1)	75.2 (1)
CNT(1)–Rh(1)–P(1)	139.1 (2)	Te–Rh(2)–P(2)	75.5 (1)
CNT(1)–Rh(1)–P(2)	136.3 (2)	P(1)–Rh(2)–P(2)	73.0 (1)
Te–Rh(1)–P(1)	75.2 (1)	C(1)–P(1)–C(2)	99.2 (6)
Te–Rh(1)–P(2)	75.3 (1)	C(3)–P(2)–C(4)	99.1 (6)
P(1)–Rh(1)–P(2)	73.1 (1)		

(c) Dihedral Angles (deg)^b

[P(1)–Rh(1)–P(2)]–[P(1)–Rh(2)–P(2)]	136.7 (3)
[Rh(1)–P(1)–Rh(2)]–[Rh(1)–P(2)–Rh(2)]	127.0 (3)
[Rh(1)–P(1)–Rh(2)]–[Rh(1)–Te–Rh(2)]	116.3 (2)
[Rh(1)–P(2)–Rh(2)–[Rh(1)–Te–Rh(2)]	116.7 (2)

^{a}CNT = centroid of Cp* ring. ^{b}String of atoms in brackets represents the atoms of a plane.

6.59; Rh, 27.52. MS (70 eV): *m/e* 740 (17%; M$^+$), 725 (100%; M$^+$ – CH$_3$), 695 (9%; M$^+$ – 3CH$_3$), 373 (3%; Rh(C$_5$Me$_5$)$_2^+$), 238 (3%; C$_5$Me$_5$Rh$^+$). ^{1}H NMR (C$_6$D$_6$): δ 3.75 (s; 3 H, CO$_2$Me), 3.71 (s; 3 H, CO$_2$Me), 2.31 (d, J_{P-H} = 10.5 Hz, 3 H, PCH$_3$), 2.00 (d,br, J_{P-H} = 2.6 Hz, 15 H, C$_5$Me$_5$), 1.75 (d, J_{P-H} = 10.5 Hz, 3 H, PCH$_3$), 1.70 (ddd, J_{P-H} = 2.9 Hz, J_{P-H} = 2.1 Hz, J_{Rh-H} = 0.4 Hz, 15 H, C$_5$Me$_5$), 1.40 (m, 6 H, PCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ –30.02 (ddd, J_{Rh-P} = 128.8 Hz, J_{Rh-P} = 6.7 Hz, J_{P-P} = 32.8 Hz), –79.84 (ddd, J_{Rh-P} = 142.9 Hz, J_{Rh-P} = 87.8 Hz, J_{P-P} = 32.8 Hz). ^{13}C NMR (C$_6$D$_6$): δ 172.20 (s, *C*O$_2$Me), 169.61 (s, *C*O$_2$Me), 97.39 (s, C$_5$Me$_5$), 95.20 (s, C$_5$Me$_5$), 49.77 (s, OCH$_3$), 49.59 (s, OCH$_3$), 22.48 (s, *C*CO$_2$Me), 22.29 (s, *C*Co$_2$Me), 14.82 (m, PCH$_3$), 9.97 (s, C$_5$(*C*H$_3$)$_5$), 9.92 (s, C$_5$(*C*H$_3$)$_5$).

11: yield 105 mg (34%); mp 250 °C dec. Anal. Calcd for C$_{30}$H$_{48}$O$_4$P$_2$Rh$_2$: C, 48.66; H, 6.53; Rh, 27.79. Found: C, 48.86; H, 6.59; Rh, 27.45. The mass spectra of **11** is almost identical with that of **10**. ^{1}H NMR (C$_6$D$_6$): δ 3.70 (s, 6 H, CO$_2$Me), 2.26 (vt, *N* = 11.8 Hz, 6 H, PCH$_3$), 2.10 (d, J_{Rh-H} = 0.3 Hz, 15 H, C$_5$Me$_5$), 1.96 (dt, J_{P-H} = 2.3 Hz, J_{Rh-H} = 0.4 Hz, 15 H, C$_5$Me$_5$), 1.40 (vt, *N* = 7.0 Hz, 6 H, PCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ –2.99 (dd, J_{Rh-P} = 158.3 Hz, J_{Rh-P} = 2.7 Hz). ^{13}C NMR (C$_6$D$_6$): δ 173.40 (vt, *N* = 17.2 Hz, *C*O$_2$Me), 96.77 (s, C$_5$Me$_5$), 92.18 (d, J_{Rh-C} = 4.5 Hz, C$_5$Me$_5$), 50.47 (s, OCH$_3$), 38.06 (dvt, *N* = 69.6, J_{Rh-C} = 14.6 Hz, *C*CO$_2$Me), 22.81 (dvt, *N* = 60.9, J_{Rh-C} = 12.1 Hz, PCH$_3$), 21.60 (s, PCH$_3$), 11.50 (s, C$_5$(CH$_3$)$_5$), 10.80 (s, C$_5$-(CH$_3$)$_5$).

Crystallographic Structural Determination for 7. Crystals of **7** were grown by layering pentane on a toluene solution. All specimens examined showed extensive interpenetrant twinning; a crystal free of twinning effects was obtained from one arm of a much larger formation. Lattice parameters (Table II) were obtained from the best fit of the angular settings of 25 reflections (23° ≤ 2θ ≤ 30°). The data were corrected for *Lp* effects, linear decay (~10%), and absorption (empirical, 256 data, ellipsoidal model).

The Te, Rh, and P atoms were obtained by direct methods (SOLV). All nonhydrogen atoms were anisotropically refined, and hydrogen atom contributions were idealized for the (μ-PMe$_2$) groups but ignored for the C$_5$Me$_5$ groups. Table III provides the atomic coordinates and Table IV selected bond distances and angles. SHELXTL software was used for all computations and served as the source for the neutral-atom scattering factors (Nicolet Corp., Madison, WI).

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); F_o/F_c tables (21 pages). Ordering information is given on any current masthead page.

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Triaqua(benzene)ruthenium(II) and Triaqua(benzene)osmium(II): Synthesis, Molecular Structure, and Water-Exchange Kinetics

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Solid salts of M(η-C$_6$H$_6$)(H$_2$O)$_3^{2+}$ (M = Ru, Os) are obtained by reacting [MCl$_2$(η-C$_6$H$_6$)]$_2$ with Ag$^+$ in aqueous solution or by the reaction of Ru(H$_2$O)$_6^{2+}$ with cyclohexadiene in ethanol. [Ru(η-C$_6$H$_6$)(H$_2$O)$_3$]SO$_4$ crystallizes in the orthorhombic space group *Pbca* with *a* = 12.892 (2) Å, *b* = 12.441 (1) Å, and *c* = 12.183 (2) Å (*T* = 125 K), and *Z* = 8. The structure was refined to 1.9% for 2168 reflections with $F_o > 3\sigma(F_o)$. The relative arrangement of the benzene ring and the three water molecules is approximately staggered, the torsional angle being 19.2 (4)°. After correction for thermal motion, average distances are Ru–C = 2.164 (4), C–C = 1.419 (5), and Ru–O = 2.117 (11) Å. The Ru–center of the benzene plane distance is 1.631 Å. Structural results obtained at 295 K agree with those at 125 K. Water-exchange rates at variable temperature and pressure were determined by line width measurements of ^{17}O NMR spectra at 4.7 T. For Ru(η-C$_6$H$_6$)(H$_2$O)$_3^{2+}$ and Os(η-C$_6$H$_6$)(H$_2$O)$_3^{2+}$ the following results are obtained: *k*(298 K), 11.5 ± 3.1 and 11.8 ± 2.0 s^{-1}; ΔH^*, 75.9 ± 3.8 and 65.5 ± 2.2 kJ mol^{-1}; ΔS^*, +29.9 ± 10.6 and –4.8 ± 6.1 J K^{-1} mol^{-1}; ΔV^*, +1.5 ± 0.4 and +2.9 ± 0.6 cm^3 mol^{-1}. The reaction proceeds via an interchange mechanism (I) where the bond-breaking contribution has only a slightly larger weight than the bond-making one. The kinetic behavior indicates a strong trans-labilizing influence of the aromatic ligand.

Introduction

Conventional procedures for the preparation of ruthenium arene complexes use the starting reagent "RuCl$_3$·*x*H$_2$O". Bis(arene) species have been originally obtained by treating ruthenium trichloride with an AlCl$_3$/Al mixture and the corresponding arene.[2] An elegant high-yield preparative route to a variety of Ru–arene complexes starts with the reaction of cyclohexa-1,3-diene with "RuCl$_3$·*x*H$_2$O" in ethanol affording the dimeric compound

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